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Preparation and characterization of ZnO thin films on InP by laser-molecular beam epitaxy technique for solar cells

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Abstract

Highly *c*-axis oriented ZnO thin films were epitaxially grown on semi-insulating ⟨1 0 0⟩ oriented InP substrates (SI-InP) held at room temperature (RT), 200°C and 300°C by laser molecular beam epitaxy (L-MBE) i.e., pulsed laser deposition. Through X-ray diffraction analysis, the material, the crystalline quality and the epitaxial lattice matching of the film were confirmed. The obtained high intense peak shows that the most preferential orientation was (0 0 2), i.e; along the '*c*-axis'. Results obtained from the optical studies indicated that the deposited film showed nearly 95% transparency and acts as anti-reflection medium. Photoluminescence (PL) study confirms the high electrical conductivity of the film and the obtained low-intensity PL spectrum indicates high O/Zn ratio. Further, the elemental peaks for Zn, O, In and P were identified by EDAX and the spectrum shows the stoichiometry of the ZnO thin films. From the optical absorption spectrum, the optical band gap and the thickness were calculated. The sheet resistance of the deposited ZnO thin films was measured for various deposition temperatures. Structural, compositional, surface morphological, optical and photoluminescence characterization results are discussed.

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1. Introduction

Due to its unique property, ZnO has been widely studied for its practical and potential applications such as transparent conducting front electrodes, flat panel displays, optoelectronic devices such as solar cells, ultra high UV, blue and green light emitting diodes (LED), piezoelectric devices, surface acoustic wave devices (SAW), oxygen gas sensors, UV laser diodes (LD). Also, ZnO is a n-type II–VI, wide band gap compound semiconductor material and

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alternative to indium oxide (ITO), analogous to gallium nitride (GaN) [1,2].

Since its properties are dependent on the method of preparation, ZnO thin film has been subject of continuous research on different preparation techniques. Each technique has its own advantages and disadvantages. Pulsed laser deposition is a promising thin film growth technology, which has been adopted in the present work to grown high-quality ZnO thin films on InP substrates for solar cell application.

ZnO has good lattice matching with the InP crystal substrates, which has high solar conversion efficiency and high radiation resistance. In this paper, the properties of pulsed laser deposited ZnO thin films on to single crystalline semi-insulating indium phosphide (InP) have been investigated in related to n-ZnO/p-InP hetero structure solar cells for space applications.

2. Experimental procedure

Semi-insulating InP single crystal wafers having $\langle 1\,0\,0 \rangle$ orientation and float glass are used as substrates for the preparation of ZnO thin films. ZnO thin films were epitaxially grown on InP substrates held at room temperature (RT), 200°C and 300°C by laser molecular beam epitaxy technique (L-MBE) i.e., pulsed laser deposition (PLD). Pulsed laser deposition has been shown to be superior to sputtering and conventional MBE for growing highly pure, low resistive, good crystalline metal oxide epitaxial thin films for opto-electronic devices and combinatorial synthesis of materials [3,4]. SI-InP single crystal wafers (grown at Hebei Semiconductor Research Institute (HSRI), Ministry of Informatics, Hebei, P.R. China) are lapped, polished with $HBr–K_2Cr_2O_7–H_2O$ solution and cleaned with trichloroethylene, acetone and methanol. The deposition of ZnO was optimized with float glass substrates using oxygen ambient at different substrate temperatures (T_{sub}) i.e: room temperature (RT), 200°C and 300°C, since deposition above 300°C has yielded low photovoltaic efficiency [5]. The pure (99.9%) ZnO powder is mixed with polyvinyl alcohol binder and hot water. Then stirred, slurred, crushed into powder, dye palletized, kept in furnace at 600°C for 3 h and sintered at 1200°C for 1 day. The ZnO target was ablated with third harmonic of "Quantel, YG 980, France, Nd:YAG laser" (355 nm, 6 ns, and 10 Hz) with energy density of 5 J/cm^2. Throughout the experiment, the laser was set at a pulse energy of 250 mJ and repetition rate of 10 Hz. Deposition chamber was initially evacuated upto 1×10^{-6} Torr pressure using a turbo molecular pump and O_2 was introduced during deposition and kept constant at 1×10^{-5} Torr. Substrate to target distance was kept at 6 cm. Throughout the deposition period, the substrate holder is rotated for uniform deposition of the ablated material.

The crystallinity of the as-grown ZnO thin films was characterized by X-ray diffraction (Philips; X-PERT-MPD, X-ray diffractometer), using Cu-K_α radiation. The composition of the ZnO thin films was analyzed by EDAX (Philips, ESEM-TMP + EDAX). SEM (Hitachi S-450 scanning electron microscope), optical spectrophotometry (Shimadzu; UV-160 and Hitachi; V.3400 UV-VIS-NIR-spectrophotometers) and photoluminescence (Hitachi; 650-10S fluorescence spectrophotometer) studies were carried out to characterize the surface morphological, optical and luminescence properties of the as-grown ZnO thin films, respectively.

3. Results and discussion

3.1. Structural characteristics

The X-ray diffraction pattern of ZnO thin films on SI-InP indicates that low T_{sub} (25°C) films are polycrystalline nature. In high T_{sub} (200°C and 300°C) films, enhancement of [1 0 0] and [0 0 2] peaks indicate that the film is approaching single crystalline nature and implying that the preferential orientation of the crystallites is along *c*-axis, which is normal to the substrate surface. This agrees well with the properties of ZnO thin films deposited onto ITO coated glass, Si [1 0 0] [6], float glass, sapphire [0 0 0 1] [7], corning glass, fused quartz substrate [8] and gallium nitride (GaN) [9]. ZnO is an interesting material in that even with low substrate heating (i.e.; at 200°C), Zn

& O atoms follow vertical packing, resulting in a single axis orientation [1]. The X-ray diffractograms are shown in Fig. 1. The ZnO belongs to hexagonal crystal system and wurtzite crystal structure. High intense and sharp peaks in X-ray diffraction spectrum further confirm the ZnO material in the stoichiometric form and the crystalline quality of the film. Also, the epitaxial lattice mismatch between the grown ZnO thin films and InP single crystal substrates is very minimum.

The full-width at half-maximum (FWHM) of ZnO [1 0 0] and ZnO [0 0 2] peaks of thin film on SI-InP and films thickness at different growth temperatures are evaluated. The decline nature of the thickness with respect to the substrate temperature indicates the reduction of growth rate. We also derived cell constant $c = 5.270$ Å along the preferential c-axis (0 0 2) orientation for 300°C film with d value as 2.635 Å. Films grown at RT, 200°C and 300°C have an average grain size of 9.2 nm, as estimated by the Scherrer method [10]. The grain

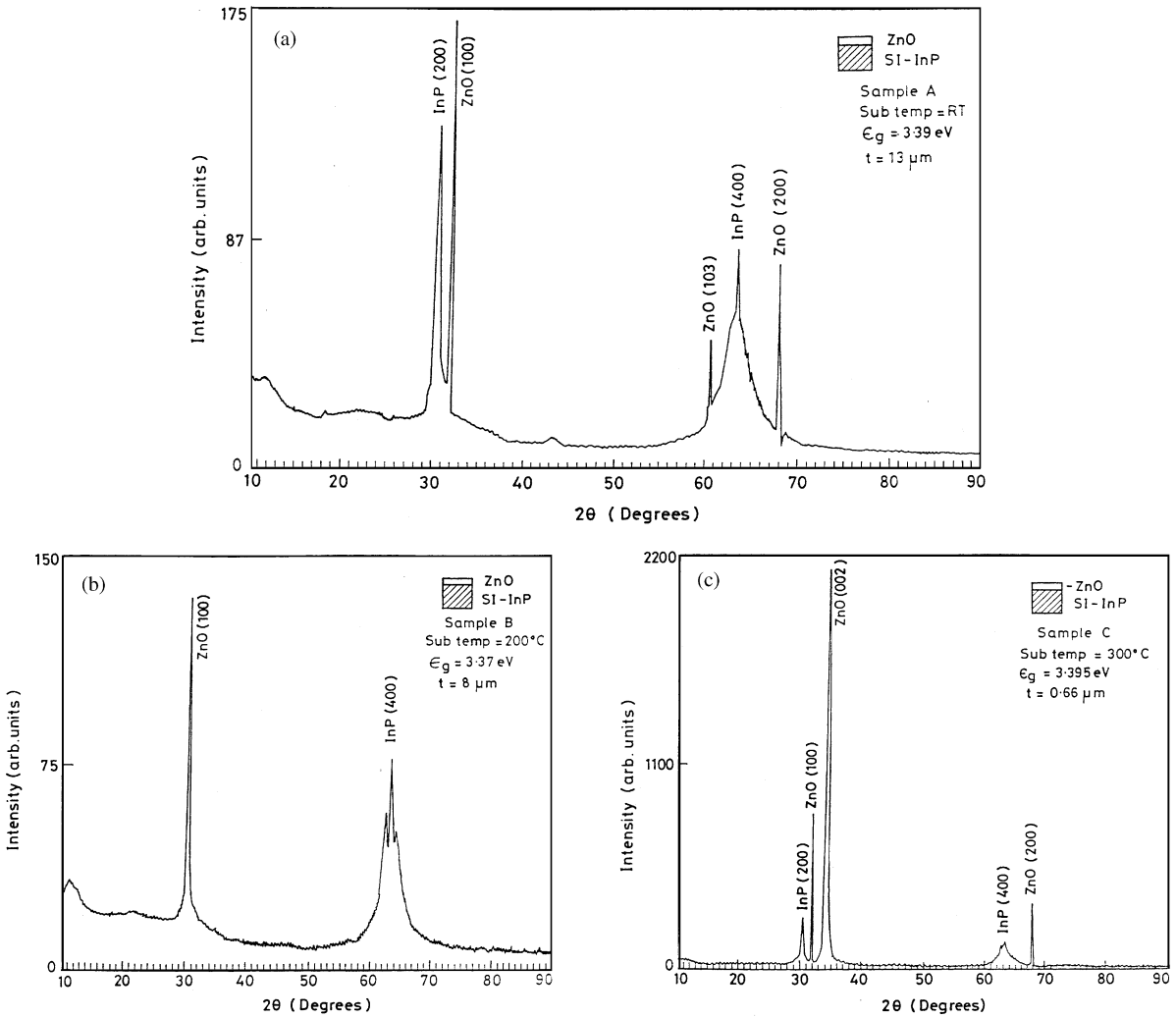

Fig. 1. The X-ray diffractograms "$\Theta-2\Theta$" scan of the epi-ZnO/SI-InP $\langle 1\,0\,0 \rangle$ structures.

size clearly indicates that our films are nanostructure materials. The observed relative intensity of the (1 0 0) and (0 0 2) diffraction peaks is greater than that given by the ASTM data (card no: 3-0888). Thus the intensity of the peak increases with increase in substrate temperature which indicates the improvization of crystalline nature of the ZnO thin films.

3.2. Compositional and electrical characteristics

The energy dispersive analysis by X-rays (EDAX) has been carried out on the optimized suitable sample of epi-ZnO/SI-InP junctions grown at 25°C. The fundamental elemental peaks of Zn, O, In and P were identified by EDAX. The spectrum further confirms the stoichiometry of the grown ZnO films. The respective EDAX spectrum is shown in Fig. 2. The samples having homogenous films were selected for sheet resistance measurements. The average sheet resistance lies in the range of 10–32 Ω/cm^2 and is a function of deposition temperature. Higher temperature deposition yields resistivities as low as $6 \times 10^{-4}\,\Omega\,cm$.

3.3. Surface morphological and growth characteristics

The surface morphology of the grown ZnO thin films on InP was analyzed by SEM. The micrograph taken for thin films deposited at room temperature confirms the granular nature of the film as well as its uniformity over the deposited area. The surface morphology of the thin film deposited at 200°C, explicitly shows the crystalline nature of ZnO, uniformity in morphology, size and distribution of the grains over the deposited surface. This confirms the effectiveness of the deposition technique [11]. The surface morphology of the deposited ZnO thin films is shown in Fig. 3. Since the crystallographic form of the thin film is largely dependent on the surface condition of the substrate, the obtained crystalline nature of the film ascertains the

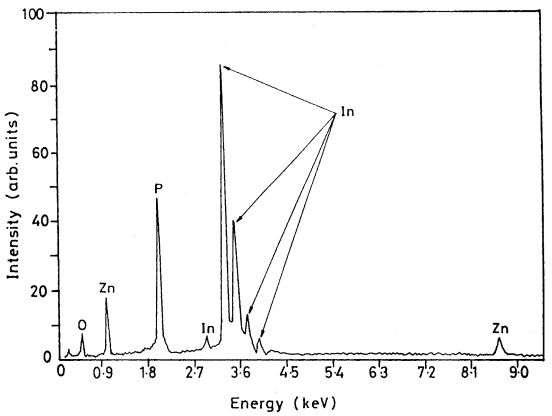

Fig. 2. The EDAX spectrum for the epi-ZnO/SI-InP ⟨1 0 0⟩ structure prepared at room temperature.

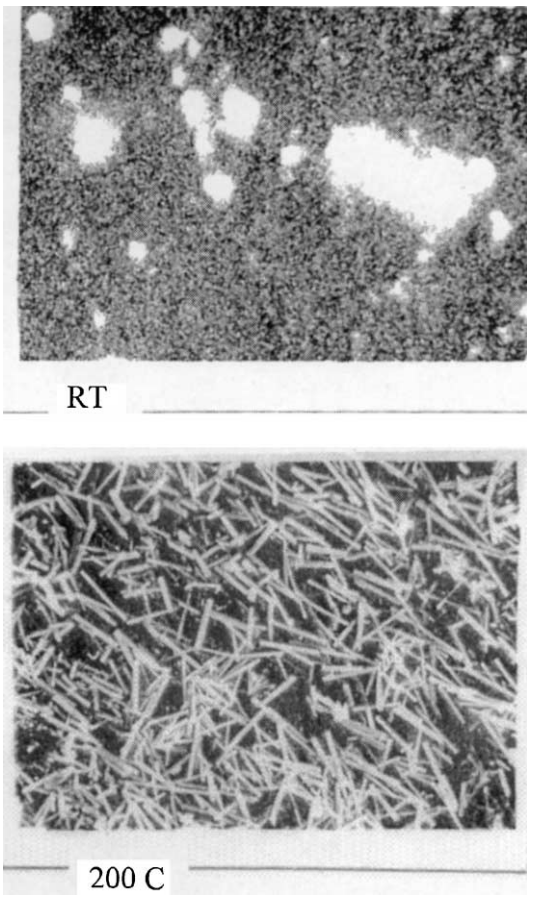

Fig. 3. The surface morphology of the ZnO thin films deposited on SI-InP substrate at room temperature and 200°C.

optimum substrate preparation method adopted in the present work.

3.4. Optical and photoluminescence characteristics

The optical studies indicated that the transmission characteristics of the films on glass substrate remain high under a variety of deposition temperatures, even for thicker (13 μm) films. The high transmission is the measure of the ability of the film surface roughness to reduce the reflectivity [12] and it is believed to arise from fine texturing at the film surface region. The increasing transmittance with deposition temperature attributed to an increase of a structural homogeneity, a decrease of the diffuse scattering and the approachment of the film composition to the stoichiometry. The refractive index (n) of the ZnO thin films on SI-InP is expected to vary through the film thickness, given sizes, impurity incorporation, deposition temperature, wavelength of incident light and stoichiometry. Since ZnO absorbs very little in the UV and visible region, the extinction coefficient (k) of ZnO thin films is considered to be zero. Obviously, a trade-off has to be found between conductivity and transparency. Transmission versus wavelength measurements were carried out in the wavelength region of 300–1100 nm. The thickness of the film was determined from the optical interference method [13]. Fig. 4 shows the thickness (μm) of the epi-ZnO thin films as a function of substrate temperatures.

The transmission of the film increases with substrate temperature. The film formed at the substrate temperature 300°C had an improved transmission of about 95% in the visible region. Fig. 5 shows the optical transmission (T%) spectrum of as-grown ZnO thin films.

The energy band gap of the films evaluated from the $(\alpha h\nu)^2$ versus $h\nu$ plots varying between 3.37 and 3.395 eV, with substrate temperatures is shown in Table 1. Further, poor reflection spectra confirm the anti-reflection property of the ZnO thin films. Thus, the transparency of the obtained films confirmed that they are appropriate for solar cell application.

Photoluminescence characterization on epi-ZnO thin films/SI-InP were carried out at room temperature. The PL spectra well agree with previous work [14] and are shown in Fig. 6. The lower intensity observed in the PL spectra indicates the high purity of the material, high electrical conductivity and high O/Zn ratio.

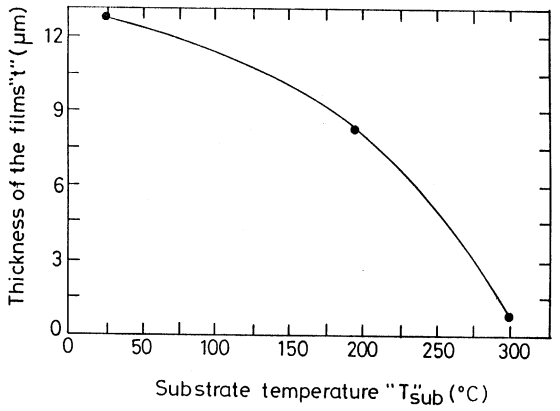

Fig. 4. The thickness (μm) of the epi-ZnO thin films as a function of substrate temperatures (T_{sub}) (°C).

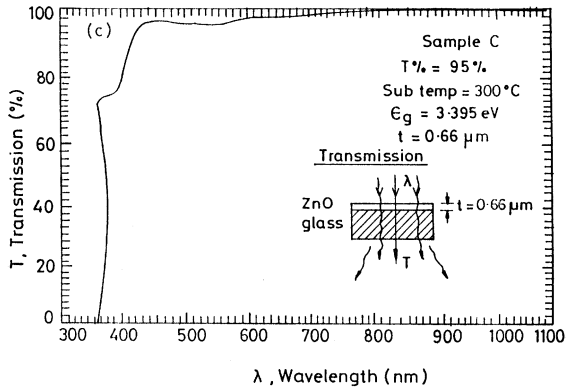

Fig. 5. The optical transmission (T%) spectrum of as-grown ZnO thin films.

Table 1
Energy gap(E_g), transparency (T%), film thickness (t) for different substrate temperatures

Substrate temperature (°C)	Energy gap (E_g) (eV)	Transparency (T%)	Film thickness (μm)
RT (25°C)	3.39	85	13
200	3.37	90	8
300	3.395	95	0.66

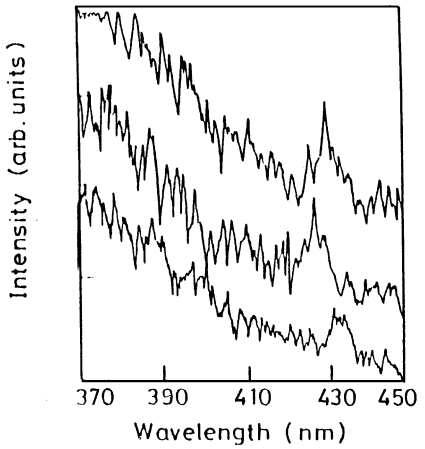

Fig. 6. The photoluminescence spectra of the epi-ZnO/SI-InP $\langle 100 \rangle$ structures at room temperature.

4. Conclusion

The high-quality ZnO thin films have been grown on SI-InP $\langle 100 \rangle$ single crystal substrates by pulsed laser deposition technique. The obtained ZnO thin films have been characterized in order to find its suitability for transparent conducting oxide (TCO) front electrodes and anti-reflection coating. The grain size clearly indicates that our films are nano-structure materials. The PLD grown ZnO thin films on InP have highly transparent conducting nature in addition to good lattice matching with out any buffer layer like GaN in the case of sapphire [9] and GaN-based III–V compounds [1] as referred in the literature. The stoichiometric and crystalline properties (as shown in X-ray diffractograms and SEM micrographs) confirm the better quality of the grown films. Thus ZnO thin film with good crystallinity, stoichiometry, surface homogeneity, high transmissibility, material purity and high electrical conductivity has been achieved.

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